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| II/98 S-40 | 11.11. -12.11.98 | A. Braun | SANS | |

SANS ON ACTIVATED GLASSY CARBON

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Electrochemically oxidised and reduced Glassy Carbon (GC) sheets were investigated with Small Angle Neutron Scattering and Electrochemical Impedance Spectroscopy. Only preliminary results will be presented in this report. It was found that the internal surface area of the oxidised GC is larger than the internal surface area of GC reduced after oxidation. It was also found that oxidised GC has a larger Electrochemical Double Layer Capacitance (DLC) than GC which is reduced after oxidation.

Electrochemically oxidised GC can be used as an electrode material for Supercapacitors. Upon oxidation, carbon is anodically dissolved, closed pores become open and the pore walls probably become decorated with surface functional hydrocarbon groups, which suppress the capacitance of electrodes, when prepared from GC. Therefore, a subsequent electrochemical reduction of oxidised GC is necessary in order to achieve a high DLC. [1].

After oxidation, the GC sheets consist of an untreated interior part with closed pores and an outer part with open pores. The samples then can be regarded as sandwiches. Thin GC sheets of 48 microns thickness, which had been pyrolyzed at 2200°C by the manufacturer, were electrochemically oxidised for 1 hour at a potential of 2.07 V vs. the saturated calomel electrode in an electrochemical cell with 3M sulfuric acid. Then an electrochemical impedance spectrum was recorded in the frequency range from 0.1 Hz to 100 kHz at a bias voltage of 0.9 V. The DLC of this sample with apparent geometrical area A as a function of the frequency, $C(f)$, was calculated from the imaginary part of the impedance Z , Z'' , according to $1/C(f) = 2 \cdot \pi \cdot Z'' \cdot A$. Figure 1 displays a plot of the DLC vs. the frequency.

A second sample was oxidized in the same way and then reduced at a potential of -0.5 V for 15 minutes. Again an impedance spectrum was recorded, of which the DLC vs. the frequency was determined, as displayed in Figure 1.

From the impedance spectra, also the diffusion resistance of the samples was determined.

It is obviously that the DLC of the oxidised GC is higher than that of the reduced GC. Another feature of the oxidised GC is that its DLC is more stable for frequencies up to 30 Hz, while the reduced GC exhibits a more pronounced decrease of DLC in this frequency range. This could be caused by the electrolyte diffusion resistance, which was measured to be nearly 40% higher for the reduced GC than for the oxidised GC.

The non treated GC with a rough flat surface has a DLC of only 100 $\mu\text{F}/\text{cm}^2$. For the treated samples, the DLC at 0.1 Hz was around 440 mF/cm^2 for the oxidised and 236 mF/cm^2 for the subsequently reduced sample. Therefore, upon reduction, the DLC decreases by a factor of 1.86. This result is in contradiction to the results mentioned in Ref. [1]. However, in this work GC with another microstructure was investigated.

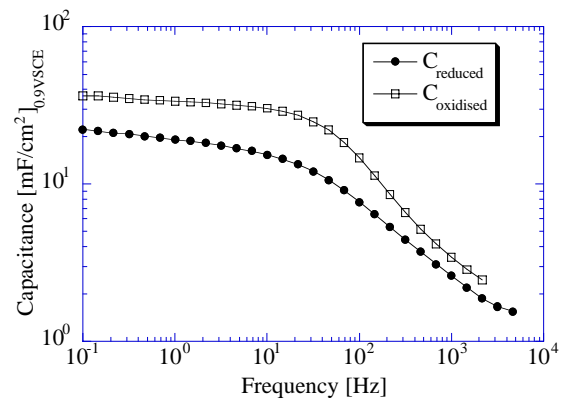


Fig. 1: Frequency response of the DLC of oxidised GC, and GC reduced after oxidation.

The GC sheets mentioned above were investigated with Small Angle Neutron Scattering, using neutrons with a wavelength of 8 Å. The scattering data gathered are still under evaluation and results will be reported later in detail. As absolute values in [barn/atom] are not yet available, we will restrict on relative values [a.u.] first.

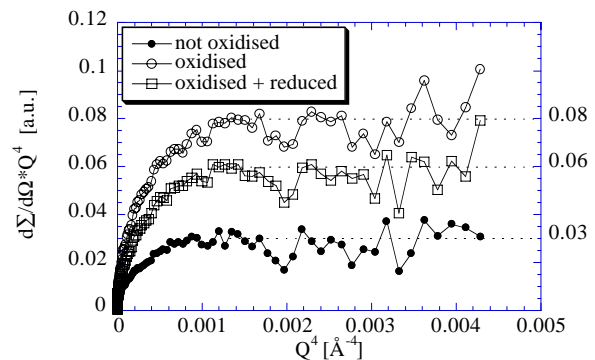


Fig. 2: Porod plot of treated and untreated GC samples. As a preliminary result, Porod plots of the scattering curves of the non treated GC material and GC treated as described above are displayed in Figure 2. The extrapolated curves for large Q values lead to the Porod constants, which are a measure for the internal surface area of the samples. Upon oxidation, the Porod constant and thus the internal surface area of the whole sample increases by a factor of around 2.7

from 0.03 to 0.08 [a.u.]. This effect may be attributed to the growth of pores during oxidation. However, after reduction the Porod constant decreases from 0.08 to 0.06 [a.u.]. These values must be corrected, because the scattering data of the treated GC sheets are obtained from sandwichlike samples. As a first rough estimation, the Porod constant of the untreated sample may be subtracted from the Porod constants of the treated samples. The ratio of the Porod constants of the oxidised film (P_{ox}) and the reduced film (P_{red}) indicate the ratio of the internal surface area of the two samples and may be estimated as follows: $(0.08-0.03)/(0.06-0.03)=1.67 > P_{ox}/P_{red} > 0.08/0.06=1.33$.

A collapse of the pore network upon the reduction may be one explanation for the decrease of the internal surface

area and the DLC. The ratio of the internal surface area of the oxidised and reduced sample corresponds roughly to the ratio of the measured DLC, which is expected. Differences could arise from the possibility that not all pores are wetted by the electrolyte and large pores are not detected with SANS. Also the higher diffusion resistance of the reduced GC could be explained by a narrowing of the pores after the pore network being collapsed.

[1] M. Sullivan, R. Kötz, and O. Haas. In *Proceedings of the Symposium on Electrochemical Capacitors*, 95-29, p. 198-209. The Electrochemical Society, ECS (1996).